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2004 J. Phys.: Condens. Matter 16 S3473

(http://iopscience.iop.org/0953-8984/16/33/007)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) S3473–S3478 PII: S0953-8984(04)75276-5

X-ray absorption spectroscopy study of chromium recovered from Cr(VI)-containing water with rice husk

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Received 20 January 2004
Published 6 August 2004
Online at stacks.iop.org/JPhysCM/16/S3473
doi:10.1088/0953-8984/16/33/007

Abstract

The characteristics of the richness in silica and the high porosity of rice husk enable its application as a good, yet cheap, heavy metal adsorbent from wastewater. This study used rice husk to sorb Cr(VI) from wastewater that contained 2000 mg Cr(VI) l^{-1}. Results of a scanning electron microscopy (SEM) experiment indicate a considerable morphology alteration of the rice husk after the sorption experiments. ^{13}C-nuclear magnetic resonance (NMR) measurements show significant decrease in intensity of all the following peaks: carbonylic, carboxylic, aromatic, polysaccharides, carbohydrates and aliphatics. The X-ray absorption near edge structure (XANES) result indicates that about 70% and 90% of the Cr(VI) sorbed on the rice husk after the 12 and 48 h sorption experiments, respectively, were in Cr(III) forms. In the 12 h sorbed rice husk sample, the chromium species distribution is 41% organic Cr(III) + 27%$Cr(OH)_3$ + 32%CrO_3, while in the 48 h sorbed one, it is 57% organic Cr(III) + 31%$Cr(OH)_3$ + 12%CrO_3.

1. Introduction

Chromium is intensively used in many industries, such as steel, alloys, electroplating, firebrick, leather tanning, dyeing, etc. Cr(VI), an oxyanion, is carcinogenic and mutagenic and has been considered as one of the 17 chemicals of the greatest threat to human health by the US Environmental Protection Agency (USEPA) (Masscheleyn *et al* 1992). In contrast, Cr(III) is a necessary micronutrient to human. Exposure to Cr(VI) can result in the perforation of the nasal septum, kidney damage, asthma, bronchitis, pneumonia, tracheal cancer, skin allergy, dermatitis, skin erosion and skin cancer. In a natural water system that is slightly acidic, Cr(VI) mainly exists in forms of CrO_4^{2-} and $HCrO_4^-$ (Richard and Bourge 1991). In neutral to basic soils, Cr(VI) is mostly in salts of CrO_4^{2-}, such as Ca CrO_4, etc, while in acidic soils it is in $HCrO_4^-$ (James and Bartlett 1983, Kotas and Stasicka 2000). Cr(III) in soils is mainly in an

insoluble form: $Cr(OH)_3$ (James and Bartlett 1983, Richard and Bourge 1991, Jardine *et al* 1999) or bound with soil humic substances (James and Bartlett 1983). Cr(III) is proposed to link to humic substances primarily through the carboxylic functional groups, and to a lesser extent through other groups such as alcoholic, phenolic, thiol, etc (Krajnc *et al* 1995).

To date, there has been very limited information available on chromium species distribution in environmental studies. The objective of this study is to sorb Cr(VI) from wastewater with rice husk. X-ray absorption spectroscopy (XAS) was used to investigate chromium species distribution in Cr-sorbed rice husks.

2. Experimental details

The rice husk was collected from central Taiwan. It contains 9.9% moisture, 21% ash, and 69% combustibles that mainly consist of lignin, cellulose and hemicellulose. As the pretreatment, it was washed with de-ionized water, dried at $105 \pm 5\,^{\circ}C$ in an oven, and finally ground to a size smaller than 50 mesh. Experiments of Cr(VI) sorption onto rice husk were carried out as follows. 100 ml solution of 2000 mg Cr l^{-1} concentration was end-to-end mixed with 5 g rice husk in a 100 ml PE bottle at a rotating speed of 30 rpm for 12 and 48 h. After the mixing, the mixture was solid–liquid separated using a N_2-pressurized filtration process. Cr concentration in the liquid phases was measured with a flame atomic absorbency spectrometer (FAAS) (Z-6100, Hitachi, Japan) and the solid phases (i.e. Cr-sorbed rice husk) were dried at $30 \pm 5\,^{\circ}C$ until the weight reached a constant. The rice husk prior to and after Cr(VI) sorption was studied with

(i) scanning electron microscopy (SEM) (XL 40 FE_SEM, Philips, Netherlands),
(ii) ^{13}C-NMR (DSX 400W, Bruker, Germany) with cross polarization magic angle spinning, that was operated at 100.46 MHz for ^{13}C nucleus with a contact time of 1500 μs, and
(iii) Cr K-edge XAS (Wiggler 17C beam line of National Synchrotron Radiation Research Center of Taiwan, which has a storage energy of 1.5 GeV and a beam current of 120–200 mA).

The XANES contains information on the Cr electronic state, while EXAFS reveals its coordination environment.

An XAS spectrum contains three regions: (i) the pre-edge region, (ii) the x-ray absorption near edge structure (XANES) and (iii) the extended x-ray absorption fine structure (EXAFS). The XANES region gives information on the electronic property of absorbing atom. The Cr(VI) pre-edge region is characterized by a strong absorption peak due to the transition of Cr 1s core electrons to its 3d orbital (Kutzler *et al* 1980, Bajt *et al* 1993, Sutton *et al* 1993). The normalized area of the pre-edge peak has been proved to be quantitatively proportional to the ratio of Cr(VI) to total Cr (Bajt *et al* 1993). The EXAFS provides information on coordination environment of the absorbing element. Coordination number, interatomic distance and degree of coordination order can generally be derived from EXAFS fitting. In this study all XAS spectra were analysed using WinXAS 2.0 software (Ressler 1998). The software can simulate a sample XANES spectrum with a linear combination of various reference spectra to quantify species, based on a least-squares procedure, in a multi-species sample, from their fingerprints in the near edge region (Ressler 1998). Partial concentration and energy correction parameters are determined for each reference compound (Ressler 1998). The latter parameter is to correct for small differences in energy calibration between sample and references because the small differences may cause big differences in the fit (Ressler 1998). References showing negative partial concentration or unreasonable energy shift at the end of the refinement process are usually absent from the sample (Ressler 1998).

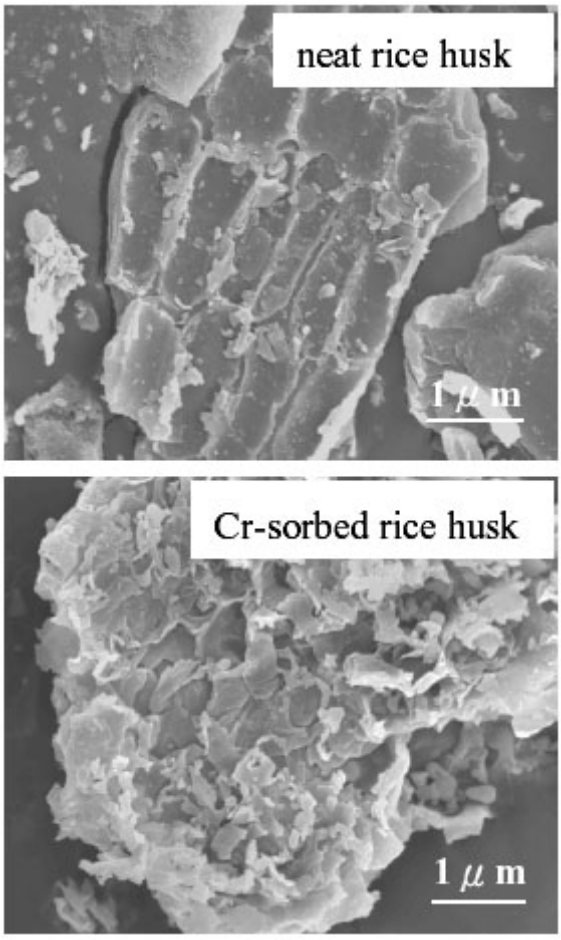

Figure 1. SEM morphologies of the neat rice husk (top panel) and the rice husk having sorbed Cr(VI) in the 2000 mg Cr l^{-1} solution for 48 h (bottom panel).

To construct a calibration curve for the FAAS measurements, Cr(III) stock solution (1000 mg Cr(III) l^{-1}, Merck) was diluted to six different concentrations (0–4.0 mg l^{-1}) and each concentration was measured for Cr in triplicates. The correlation coefficient (r^2) for the calibration curves was required to be greater than 0.995. A quality control (QC) standard solution of certified Cr concentration was routinely measured to check the validity of the calibration curve for each 20 unknown sample measurements. Only the recovery yield of 80–120% was acceptable, otherwise a new one was re-constructed. To determine the method detection limit (MDL), an unknown sample was continuously diluted until the FAAS signal-to-noise ratio was just greater than 3.0. Three times the standard deviation of 12 replicate measurements of the diluted unknown sample was considered as the absorbency for MDL. The chromium MDL was determined to be 32 μg l^{-1}.

3. Results and discussion

Figure 1 shows the SEM morphologies of the neat rice husk (see top compartment) and the rice husk having sorbed Cr(VI) in the 2000 mg Cr l^{-1} solution for 48 h (see bottom panel).

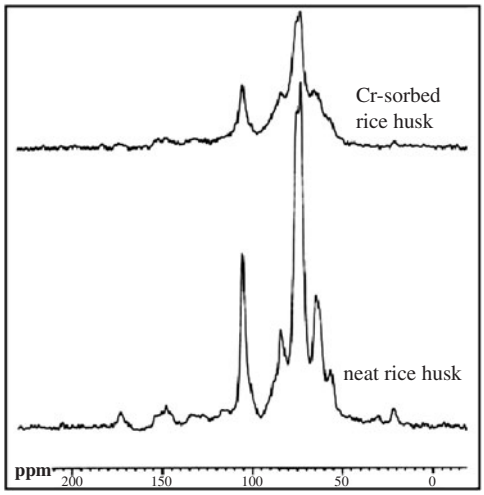

Figure 2. ^{13}C-NMR spectra of the neat rice husk and the rice husk having sorbed Cr(VI) in the 2000 mg Cr l^{-1} solution for 48 h.

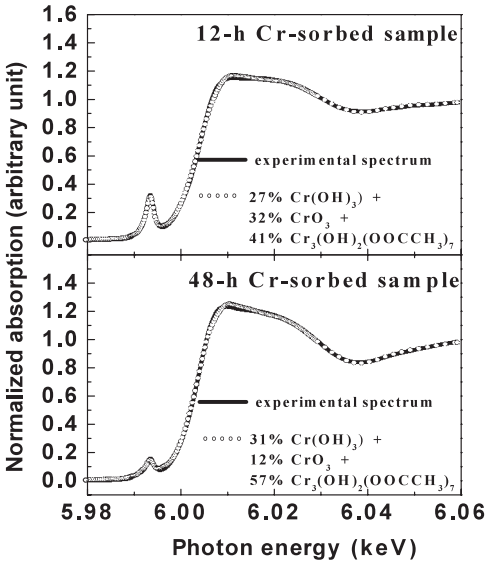

Figure 3. Results of the simulation of sample XANES spectra (top: the 12 h sample; bottom: the 48 h one) with that of three references: CrO_3, $Cr(OH)_3$ and $Cr_3(OH)_2(OOCCH_3)_7$.

Table 1. Relative peak area (arbitrary unit) in different chemical shift regions of the ^{13}C-NMR spectra of neat rice husk and the rice husk having sorbed Cr(VI) in the 2000 mg Cr l^{-1} solution for 48 h.

	Chemical shift (ppm)				
Sample	200–160 carboxylic	160–110 aromatic	110–90 polysaccharides	90–50 carbohydrates	50–0 aliphatic
Neat rice husk	100[a]	353.3	471.9	1957.4	191.3
Cr-sorbed rice husk	92.2	264.8	288.6	1072.7	99.3

[a] 100 is the selected peak area basis; the others are compared with it.

It indicates that the surface structure of the neat rice husk was corroded or oxidized after the Cr(VI) sorption. This may be attributed to the considerable oxidation capability of Cr(VI) toward rice husk. It is inferred based on these pictures that part of Cr(VI) was chemically reduced to Cr(III) once it was in contact with the rice husk. However the SEM results do not give information on either the ratio of trivalent Cr to total sorbed Cr or that on Cr(III) speciation.

Figure 2 presents the ^{13}C-NMR spectra of the neat rice husk and the rice husk having sorbed Cr(VI) in the 2000 mg Cr l^{-1} solution for 48 h. The chemical structures characterized by the chemical shifts (in ppm) are: carbonylic and carboxylic functional groups in the region of 200–160 ppm, aromatic structure in 160–110 ppm, polysaccharides in 110–90 ppm, carbohydrates in 90–50 ppm, and aliphatic structure in 50–0 ppm. At first glance the NMR results show considerable decrease in the height of most peaks after the sorption experiment for 48 h. Further examination reveals that, after Cr(VI) sorption, the peak height in the region of 110–0 ppm is much more reduced than that in the 160–110 ppm region. Area quantification of these peaks is performed by assigning 100 units to the 160–110 ppm region of the neat rice husk, and the other peaks were normalized to it. The quantification results are listed in table 1.

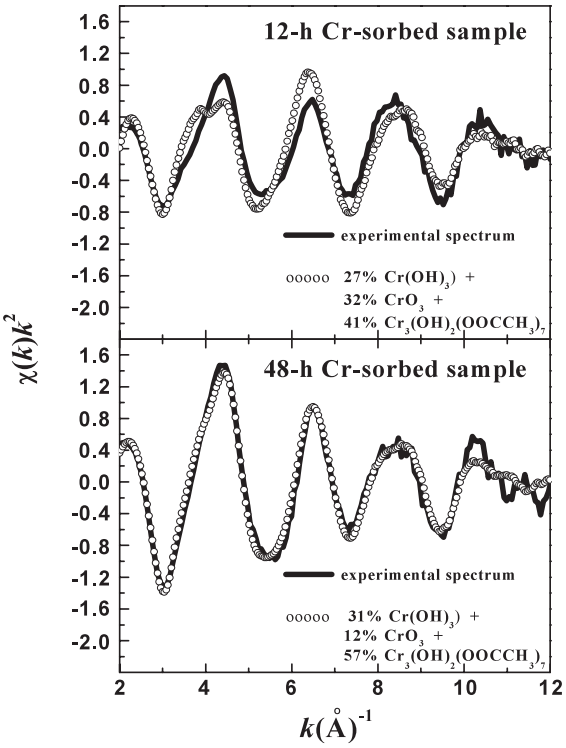

Figure 4. Simulation of the sample EXAFS spectra of Cr-sorbed rice husks with that of three references: CrO_3, $Cr(OH)_3$ and $Cr_3(OH)_2(OOCCH_3)_7$.

As shown in table 1, the peak area of the 200–160 ppm region (i.e. carbonylic and carboxylic functional groups) of the Cr(VI)-sorbed rice husk is 92.2% of that of neat rice husk. The result suggests that because Cr(VI) is an oxyanion that is negatively charged, the opportunity for the oxyanion to have access to the carbonylic and carboxylic functional groups would be low due to the electrostatic repulsion between the oxygen in the oxyanion and that in the carbonylic and carboxylic groups. Thus oxidation of these functional groups would be minimal.

The peak area of the 160–110 (aromatics) and 110–90 ppm (polysaccharides) regions of the Cr(VI)-sorbed rice husk decreases to 75% and 60%, respectively, of that of the neat rice husk. For the 90–50 (carbohydrates) and 50–0 ppm (aliphatics) regions of the Cr(VI)-sorbed rice husk, their respective peak areas are about 50% of that of the neat rice husk. These results indicate that the chemical structure of carbohydrates (90–50 ppm) and the aliphatic structure (50–0 ppm) are weaker than the aromatic structure (160–110 ppm) and polysaccharides (110–90 ppm), thus they are easier to be oxidized by Cr(VI).

Figure 3 shows the simulation results of sample XANES spectra (top panel: the 12 h sample; bottom: the 48 h one) simulated with that of three references: CrO_3, $Cr(OH)_3$ and $Cr_3(OH)_2(OOCCH_3)_7$. $Cr_3(OH)_2(OOCCH_3)_7$ is chosen as a reference compound to model the chemically sorbed Cr(III) through ionic exchange. $Cr(OH)_3$ is selected as a reference to represent the physically deposited Cr(III) on the surface of the rice husk after the chemical reduction of Cr(VI). The solid curve in figure 3 is the sample experimental XANES and the open circle curve is the simulated one. The percentages of the three

chromium reference compounds listed in each compartment are the XANES simulation results. The simulation results indicate that chromium species distribution in the 12 h sample is 41% $Cr_3(OH)_2(OOCCH_3)_7$ + 27%$Cr(OH)_3$ + 32%CrO_3, while the 48 h sample has 57% $Cr_3(OH)_2(OOCCH_3)_7$ + 31%$Cr(OH)_3$ + 12%CrO_3. Sorption for a longer period of time reduced the per cent of Cr(VI), 12% in the 48 h sample versus 32% in the 12 h one.

Figure 4 presents the simulation of the corresponding EXAFS spectra for the Cr-sorbed rice husk samples. The simulation curves were obtained by linearly combining all reference EXAFS in the weight per cents resulting from their corresponding XANES fitting. The results of the simulation are satisfactorily.

4. Conclusion

Considerable chemical reduction of Cr(VI) by rice husk was achieved. Sorption for 48 h chemically reduced 88% of sorbed Cr(VI) into Cr(III), and 68% for 12 h. The sorption capacity of rice husk toward chromium for 48 h was about 20 000 and about 12 000 (mg Cr) (kg rice husk)$^{-1}$ for 12 h. Rice husk has great potential to sorb Cr(VI) from wastewater.

For the 12 and 48 h sorbed rice husk samples about 41% and 57%, respectively, of the sorbed chromium was in organic form that is represented by $Cr_3(OH)_2(OOCCH_3)_7$. This Cr(III) was considered to link to rice husk through $-COO^-$ and $-O^-$ groups via ionic exchange with a proton. By contrast, $Cr(OH)_3$, accounting for about 30% of the sorbed chromium in both samples, was suggested to merely deposit on rice husk.

Acknowledgment

We thank the staff at NSRRC for their support in the experiment.

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